

Ignition Studies

Part VII - The Determination of Autoignition Temperatures of Hydrocarbon Fuels

WILBUR A. AFFENS AND HOMER W. CARHART

*Chemical Dynamics Branch
Chemistry Division*

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associated with autoignition, such as cool flames, zones of nonignition, multiple ignition, ignition delay, and hot-surface ignition, are defined and discussed. The numerous experimental and other factors which may influence autoignition temperatures are discussed, and their relations to autoignition phenomena are described. Some of the factors are chemical structure and composition, fuel-air ratio, concentration of oxygen, surface-volume ratio, geometry of the containing vessel, and pressure.

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IGNITION STUDIES, PART VII — THE DETERMINATION OF AUTOIGNITION TEMPERATURES OF HYDROCARBON FUELS

BACKGROUND

In the last few years the Navy has become concerned with the relative flammability hazards of Navy Special Fuel (NSFO) and Navy Distillate (ND) fuel and therefore has a particular interest in the autoignition temperatures (AIT's) of these fuels [1]. Recent disasters on major vessels such as USS *Roark* and USS *Kitty Hawk* due to ignition of lubricating oils that sprayed onto hot surfaces have heightened this concern. Therefore, it was desirable to study the various phenomena that relate to and influence autoignition. The present report gives some of the results of this investigation.

INTRODUCTION

Autoignition (also called *spontaneous ignition* or *autogenous ignition*) is a complex process, and the determination of AIT or SIT (spontaneous ignition temperature) can yield results which are subject to varying interpretation, depending on the method and apparatus used to make the determination. For these reasons, attention must be focused on the methods for the determination of AIT.

There is no AIT requirement in the current military specifications for either NSFO [2] or for ND [3], nor is there one for JP-4 and JP-5 jet fuels [4]; therefore, no "official" method is specified for its determination. However, the American Society for Testing and Materials (ASTM) has a tentative method for the determination of "Autoignition Temperature of Liquid Petroleum Products" [5] which may be used for this purpose. The ASTM method is a static, "heated-crucible" type of procedure, which is the common way to determine AIT in air at atmospheric pressure. In the ASTM method, a 200-ml glass Erlenmeyer flask is heated uniformly in an oven to a given temperature, and a small, specified quantity (usually about 0.07 to 0.2 ml) of the fuel is injected into the flask by means of a hypodermic syringe. If an ignition occurs, the test is repeated at a lower temperature. The lowest temperature at which an ignition occurs under the test conditions is the minimum autoignition temperature or, more simply, the AIT. However, the previous comments on the subjectivity of the AIT determination also apply to the ASTM method. The ASTM itself [6] states this as follows: "Autogenous ignition temperature is an empirical value. It varies with the nature of the container, the concentration of the vapor in air, and with other conditions. The operator needs considerable experience to obtain test conditions that give minimum ignition temperature." For these and other reasons it can be seen that wide discrepancies can occur among AIT values of the same fuel if there are differences in either apparatus, method, or a combination of these. Furthermore, since laboratory test conditions are usually quite different from actual situations, an even wider gap can exist between laboratory AIT values on the one hand, and the actual temperatures which would be necessary for an autoignition to occur under actual conditions, for example, aboard ship when a liquid fuel leaks onto a hot steam pipe.

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A study of the reasons behind these differences should lead to more meaningful AIT data, and to proper interpretation of data.

AUTOIGNITION PHENOMENA

There are many interesting and important phenomena associated with the complex processes of autoignition, such as *cool flames*, *multistage ignition*, *zones of ignition and nonignition*, and *ignition delay*. Actually, these phenomena are the chief reasons for the difficulties in the AIT determination. One immediately becomes involved with some of these phenomena when he attempts to define AIT. Autoignition temperature may be defined as that minimum temperature at which a combustible material would ignite in air without the assistance of a spark or flame in the experimental apparatus employed. *Hot surface ignition temperature*, a related autoignition property, is the lowest temperature at which a specified hot surface will ignite a droplet of fuel that falls upon it. Hot surface ignition temperatures are not as reliable as conventional AIT values and usually are much higher because of uncontrolled loss of vapor and heat after the droplet hits the surface.

Some ignition and related terms are defined in the glossary at the end of this report. The key concept in these definitions, of course, is *ignition*, the interpretation of which is very subjective; accordingly, it is a difficult word to define. Ignition is associated with the process of the setting on fire of a combustible mixture or, in other words, with the process of flame initiation. Flames, in most cases, are defined as highly exothermic reactions between fuel vapors (or gases) and an oxidant (in this case, oxygen) resulting in both the rapid generation of combustion products at relatively high temperatures (generally above about 1100°C) and the emission of light. Accordingly, by using observable phenomena as indicators, ignition has been defined as "visible and/or audible combustion observable under ordinary laboratory conditions" [7]. From the point of view of an AIT determination, there are two weaknesses in this definition. First of all, depending on the composition of the fuel-air mixture, under certain circumstances mild or weak ignitions may occur which would not be observable under ordinary laboratory lighting conditions but which would be observed in total darkness. Furthermore appreciable time delays sometimes occur between the time the sample is injected into the reaction vessel and the moment when ignition actually takes place. The delay depends on the nature of the fuel mixture and on temperature and means that some ignitions may be missed if the observer does not wait long enough for them to occur. Any AIT method which does not take these factors into account may lead to serious discrepancies in results. A discussion of some of these factors follows.

Weak Ignitions

Under certain circumstances, particularly when smoke is generated by the preignition reactions, weak ignitions are not readily observable under ordinary laboratory conditions. For this reason the ASTM [5] has an additional requirement that the determination be run in a darkened room. Darkness would help in the detection of some weak ignitions, so that one might expect to obtain lower results than those determined in an undarkened

room. However, "darkened" is a relative term, since there are many degrees of darkness, representing a wide latitude of lighting conditions. Some weak ignitions require almost complete darkness to be observed.

Cool Flames

A cool flame is an important and complex ignition phenomena, which will not be discussed in detail here, associated with multistage ignition. For example, it has been shown that in many instances *hot flame* ignition is the result of a process of at least two stages. The first of these two stages is a relatively low temperature phenomenon — the *cool flame* ignition — whose products are responsible for the later ignition stages. A cool flame is a faint pale blue luminescence and occurs under certain conditions during degenerate branching reactions of early combustion. The pale blue light, which is due to fluorescence of excited formaldehyde, is not accompanied by a large heat release. A cool flame can be observed only in almost total darkness and with eyes well adjusted to the darkness.

The occurrence of cool flames depends on the composition and concentration of the fuel and on oxygen concentration. These phenomena were studied in earlier NRL work [7-10]. For example, a delineation of zones of cool flame, hot flame, and negative ignition is shown in a plot of oxygen concentration versus temperature from this earlier work [8] for a typical hydrocarbon, n-octane (Fig. 1). The area of positive ignition

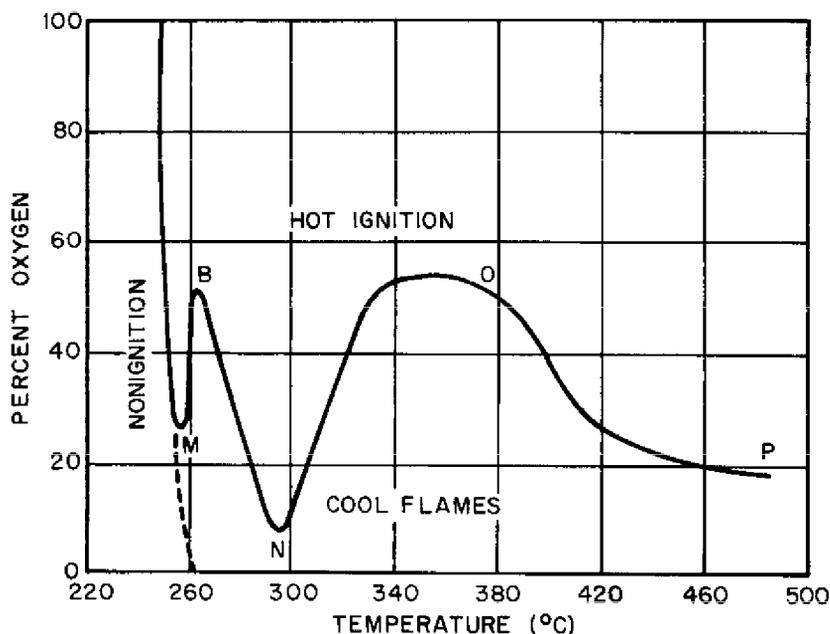


Fig. 1 — Prototype ignition curve (n-octane) [8]

(visible and/or audible combustion) lies above and to the right of the ignition curve. In the area labeled "cool flames" a reaction occurs which can be seen only in almost total darkness or detected by means of a thermocouple response. To the left is the area of nonignition in which the oxidation reactions proceed too slowly for an ignition to result. The appearance of minima or lobes at M and N and maxima at B and O is typical of many hydrocarbons; the locations of these points depend on several factors including the nature of the fuel, the size, geometry, and nature of the ignition chamber, and atmospheric pressure. Although the curve delineates the ignition zones as a function of oxygen concentration and temperature, for most purposes our interest is concerned with air (about 21% oxygen). By examining this graph along a horizontal line of constant oxygen concentration (just above the 20% line) in the figure, we will note (for the particular apparatus which was used) that the line intersects the curve at about 280°C, which in this case is the AIT. With ignition determinations at gradually increasing temperatures, positive ignitions would continue to occur until about 310°C. Above this temperature the 21% line shifts into the cool flame zone and under ordinary AIT procedures would be unobserved and hence reported as "negative." At about 450°C, positive results would again occur. We now see that in this case it is possible to have two distinct "minimum AIT" values, 280° and 450°, depending on the starting temperature.

We can now have some insight into the problems of determining accurate AIT values. First, there are compounds which may have two (or more) lobes intersected by the air line, with the result that there are alternating negative and positive regions and two (or more) "AIT" values. Furthermore, under certain conditions, the curve can be shifted. A larger chamber, for example, can cause the curve in the figure to shift downward and to the left. If the point M is moved a bit lower, the 21% line would intersect this first lobe, so that the minimum AIT in that case would be about 250°C.

In Table 1 are shown actual examples of zones of spontaneous ignition (Pos.) and "nonignition" (Neg.) in air for two fuels, NSFO and n-hexadecene. They represent alternating positive and negative* results as a traverse is made through the curve by the 21% air line, as shown in Fig. 1. The data demonstrate one of the major difficulties in obtaining a minimum spontaneous ignition temperature in air for some hydrocarbon fuels.

From the point of view of safety, it is desirable to be able to determine a true minimum AIT. Since cool flames are precursors of hot flame ignitions, and since transitions into hot flames can easily occur, either type of ignition should be considered as a "positive" ignition. For these reasons, it would be desirable to have a means of detecting cool flames; present AIT methods could be modified to make this possible. A sensitive, fast-response thermocouple in the vapor mixture of the flask connected to a suitable recorder might serve this purpose. A plot of temperature versus time for n-hexane in air from earlier NRL ignition studies [11] is shown in Fig. 2. The very steep slope of the curve is the signal that ignition has taken place; the minimum temperature where such a spike occurs may be considered as the spontaneous ignition temperature. It may be interpreted as

*In a well lit room the observations appear to be negative, but in reality "cool flames" are present, as can be seen in Fig. 1.

Table 1
Zones of Spontaneous Ignition (Pos.) and Non-Ignition
(Neg.) in Air

Navy Special Fuel Oil (Sample NRL-71-7)*		n-Hexadecene**	
Temperature Range (°F)	Result	Temperature Range (°F)	Result
Below 473	Neg.	Below 493	Neg.
473-479	Pos.	493-505	Pos.
480-486	Neg.	506-518	Neg.
487-542	Pos.	519-613	Pos.
543-548	Neg.	614-691	Neg.
549-571	Pos.	Above 692	Pos.
572-580	Neg.		
581-585	Pos.		
586-632	Neg.		
633-659	Pos.		
660-666	Neg.		
Above 667	Pos.		

*ASTM Method D 2155-66 [5]

**21-ml reaction chamber [8]

meaning that at a temperature below the ignition temperature, the rate of heat generation by the exothermic oxidation reactions is less than the rate of heat loss to the surroundings. At ignition, this rate of heat generation just counterbalances the rate of heat loss, and this imbalance results in a rapid temperature increase and an interrelated exponential increase in reaction rate.

Composition and Chemical Structure

Perhaps the most interesting factor influencing AIT is the composition and chemical structure of the fuel. Knowledge of the effect of composition and chemical structure is helpful for predicting differences in AIT for different types of fuel or fuels which have been contaminated, and for explaining unusually high or low AIT results. The approximate relationship between octane rating and the minimum ignition temperature in pure oxygen is known [10], as is the approximately inverse relationship between cetane number and AIT. In general, fuels with high AIT values have high octane numbers and low cetane numbers. Compounds or fuels which are more resistant to vapor phase oxidation (lower cetane numbers) such as isooctane or the more highly branched members of the hexane

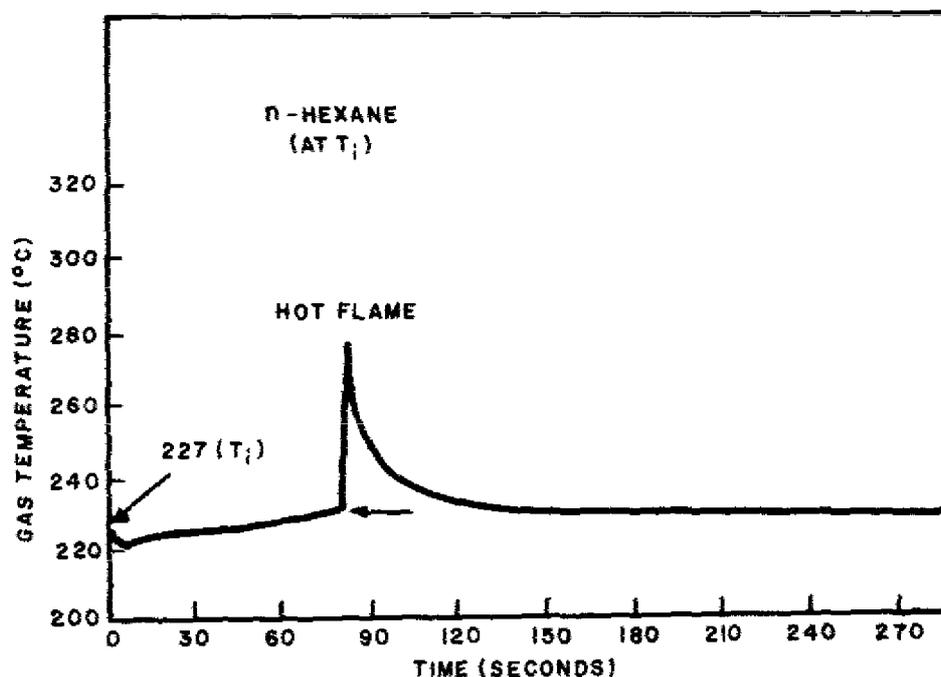


Fig. 2 — Temperature-vs-time ignition curve for n-hexane in air at its auto-ignition temperature [11]

isomers display curves which are displaced upward and to the right, so that they have higher AIT values. This is illustrated in Figs. 3 and 4 [8].

For pure hydrocarbons, certain generalizations may be made concerning their ease of ignition as a function of their chemical structure [8,11]. For example, AIT increases with decrease of carbon number in a chain and with increase in chain branching, cyclization, or aromaticity. Mixtures of two or more different hydrocarbons show ignition tendencies which are in general influenced by the more readily ignitable component, although this is not always the case.

Ignition Delay

The phenomenon of *ignition delay* is another factor in the spontaneous ignition process. If a liquid fuel droplet is introduced into a heated air chamber whose temperature is at or above the ignition temperature, it should ignite. It will be observed however that there is generally an interval between the time of the introduction of the fuel droplet and the actual ignition. For hydrocarbons in air, this delay may be as short as a fraction of a second or as long as many minutes depending on the temperature and on the composition and chemical structure of the hydrocarbons in the fuel.

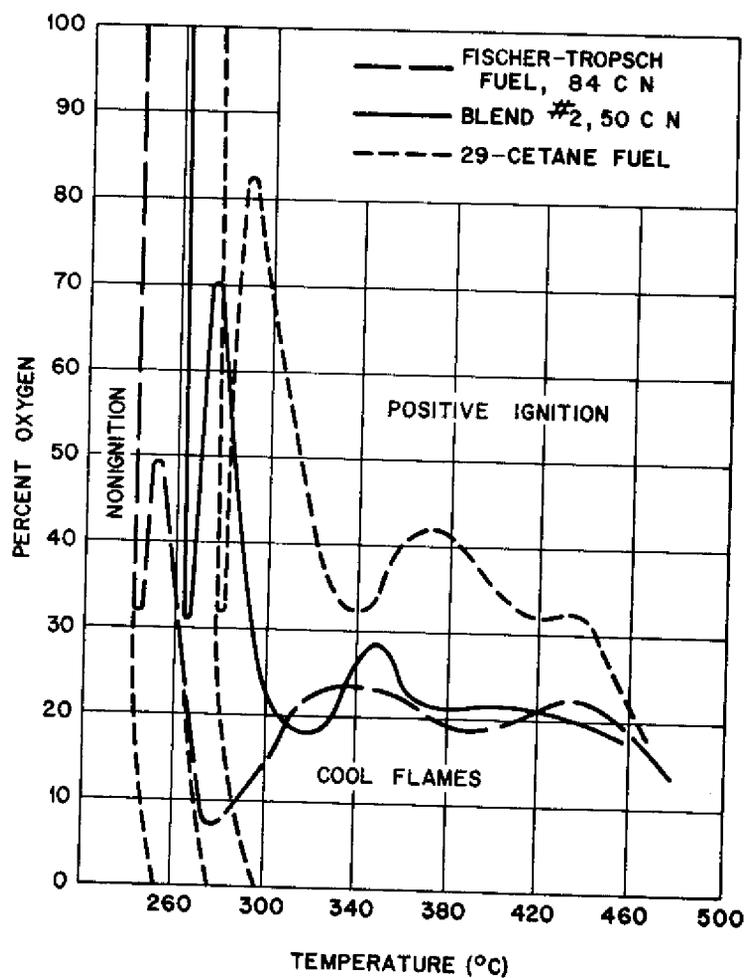


Fig. 3 - Ignition curves for fuels of different cetane number [8]

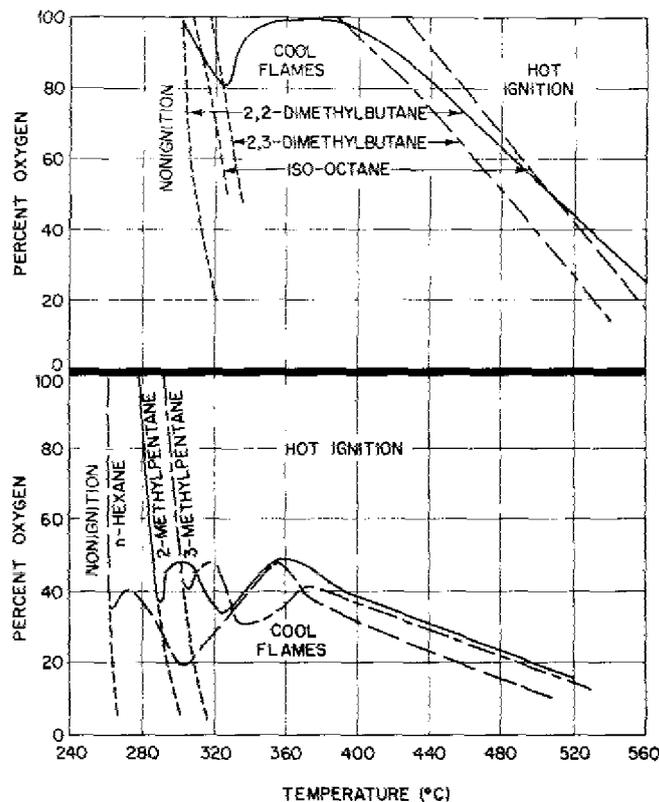


Fig. 4 - Relationships of structure to zones of ignition [9] for the isomeric hexanes

The ignition delay is defined as the time interval between contact of an oxidant with a combustible and the ignition. The delay, or induction period, consists of two components: a "physical" delay and a "chemical" delay. The physical delay is the time for the droplet to evaporate, diffuse and mix with the air, and heat up to chamber temperature. The chemical delay occurs after the contact has been made between the fuel and oxygen, and involves the kinetics of the chemical reactions which form the critical concentrations of free radicals and other intermediates which are necessary for ignition. This delay, which decreases with increasing temperature, is the more meaningful of the two, since it is a function of the chemical reactions which are taking place.

In those cases where the induction time is long, it is possible for an operator to miss a positive ignition because he did not allow sufficient time for it to occur. The ASTM procedure [5], for example, requires a 5-minute wait before a negative ignition is recorded. It is possible however in the case of certain hydrocarbon mixtures to have ignition delays in excess of 5 minutes, so that such ignitions would be unnoticed. For example, it was shown in earlier work [11] that cycloparaffins exhibit unusually long ignition delays, up to almost 9 minutes for cyclohexane. Time therefore is an additional variable in the determination of AIT, and if insufficient, may lead to differences in AIT results. There

is however a means to avoid this type of error, since it is possible to measure ignition delay as a function of temperature. If ignitions are observed at temperatures above the AIT and the delay time measured, it will be found that as temperature decreases, the ignition delay for each subsequent ignition will increase and that it will vary continuously and smoothly regardless of zones of hot and cool flame ignition. A curve of ignition delay against temperature for n-hexadecene-1 from earlier NRL work [8] showing this behavior appears in Fig. 5.

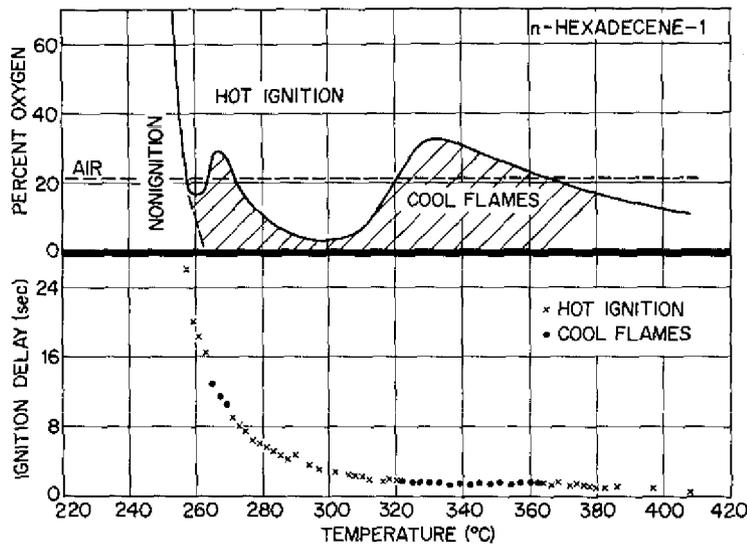


Fig. 5 — Relationship of ignition delays to zones of ignition [8]

A plot of ignition delay time (t) versus temperature (T) is helpful in determining AIT. In previous work [12] it was shown that a plot of reciprocal ignition delay time versus T is linear in the vicinity of the AIT, a fact that may be used for guidance in determining AIT (Fig. 6). These data show that it may be possible to make use of this ignition-delay-and-temperature relationship to obtain a more meaningful minimum spontaneous ignition temperature. By extrapolation of the curves to $1/t = 0$, one may define a minimum spontaneous ignition temperature value. Since the graph goes through both hot- and cool-flame data points, the extrapolated value does not place a premium on direct observation of cool flames.

Fuel-Air Ratio (Sample Size)

An important factor in the determination of AIT is the size of the sample or charge, since this determines the fuel-air ratio in the flask. Mixtures which are "rich" or "lean" usually ignite at higher temperatures than the "minimum" AIT, which generally is at a fuel-air ratio rather close to stoichiometric [8]. A plot of AIT versus sample charge will

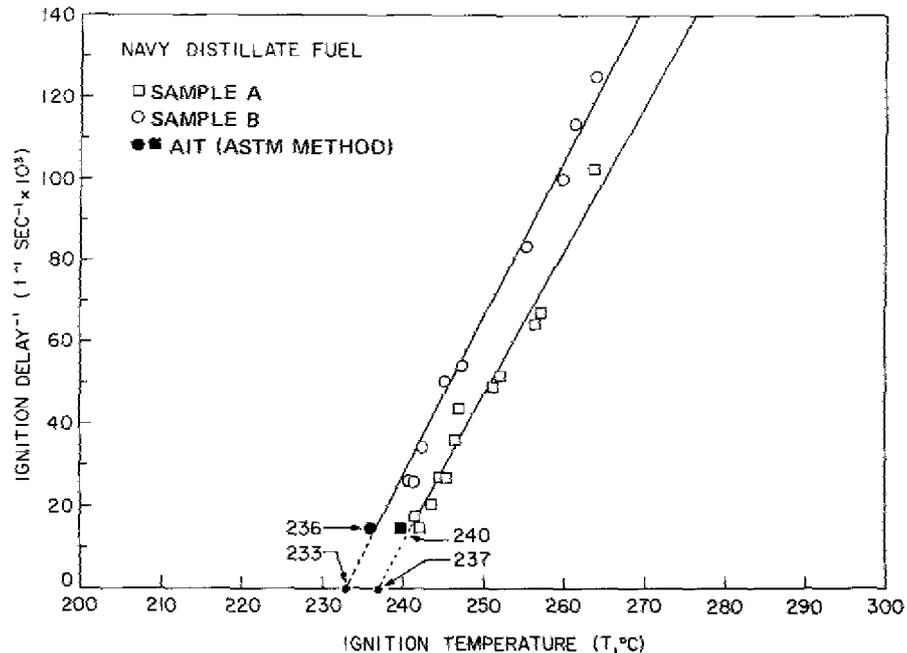


Fig. 6 — Reciprocal ignition delay versus ignition temperature for ND fuel [12]

show a minimum in the curve, and this must be taken into account in the determination of the minimum AIT. The ASTM procedure makes provision for this by requiring that sample size be varied in prescribed increments both above and below the standard sample size of 0.07 ml which is used to obtain the initial trial AIT value. It is important in AIT determinations that this "titration" be made.

Surface-Volume Ratio

If one determines AIT by a given method, but varies the size of the container, it will be observed that AIT decreases with increasing vessel size (volume). Actually the surface area of the container and its geometry are related factors, so that AIT is a function of surface-volume ratio (S/V). In general, for a given type of container, S/V decreases with volume, so that AIT decreases with decreasing S/V.

Setchkin [13] measured AIT for several fuels in spherical flasks of different sizes varying from 8 ml to 15 liters. He found that AIT decreased with volume but that the rate of decrease fell off rapidly with increasing volume. The larger flasks (> 1 liter) were awkward and bulky to work with and took longer for temperature adjustment; accordingly, for other studies he elected to use a 1-liter flask as a compromise, since above this size the temperature reduction was relatively small. The ASTM employs a 200-ml Erlenmeyer flask, which, because of its relatively small size, may tend to give higher results than those obtained by means of the Setchkin 1-liter flask. Setchkin reported that AIT values in the

200-ml flask were generally higher than those obtained by the use of the 1-liter flask, ranging from 2° to 28°C depending on the fuel. Setchkin used a vapor-phase thermocouple to detect his ignitions, and it is probable that if he had made his observations visually in a semidarkened room (without the thermocouple), the differences would be greater (as stated previously) because of shifts of the lobes of the ignition curves. For example, in the ignition plot for the isomeric hexanes and isooctane shown in Fig. 4, the n-hexane curve can be used to illustrate the significance of lobe shifting. If we find the intersection of the 21% oxygen line (air) in the figure, it intersects the n-hexane curve at about 300°C, which in accordance with the method used would be reported as the AIT. However, if a smaller container had been used for this determination, there would have been a slight upward shift of the curve. In that case, the 21% line might completely miss the lobe, and the first hot ignition would occur at about 450°C, where the curve for n-hexane again is intersected by the 21% line. In that case, the AIT would be reported as 450°C, a difference of about 150°C. Discrepancies in AIT data found in the literature may sometimes be due to this phenomenon. For example, in Table 2 are shown data from standard German [14] and American [15] references. The compounds in the table were deliberately selected to emphasize the discrepancies, which are undoubtedly due to differences in experimental methods. From these findings, it would seem advisable to modify the ASTM method so that a larger flask could be used. The use of a 500-ml spherical flask as a compromise is being investigated by an ASTM cooperative study.

Table 2
Comparison of SIT (°C)

Compound	Nabert/Schön	NFPA-325M
Acetaldehyde	140	185
Acetone	540	465
Allyl chloride	390	485
n-Butyl acetate	370	425
Ethyl alcohol	425	365
Gasoline	ca. 250	280-455
Methane	650	540
Methyl alcohol	455	385
Tetrahydrofuran	260	321

Miscellaneous Factors

Among other factors which may affect AIT results are oxygen concentration (mentioned under the discussion on cool flames), atmospheric pressure, surface effects (catalysis), inert diluents, and additives (both promoters and inhibitors). Since changes in atmospheric or total pressure change the oxygen partial pressure, it might be expected that the relationship of pressure and temperature (Fig. 7) would be similar to the relationships of oxygen concentration and ignition temperature discussed previously (Figs. 1, 3, 4, and 5). A plot of NRL ignition data superimposed on pressure data of Maccormac and Townend [16] for

n-octane is shown in Fig. 7. The Maccormac and Townend data were obtained with air at various pressures in a closed chamber and are plotted on an oxygen partial pressure basis against the NRL data from Fig. 1. It will be noted that the similarity of the two curves is surprisingly good, particularly in the proximity of the inflection points. In many instances the effect of these factors may be small, but in other cases these parameters may cause shifts in the ignition curves (Fig. 1); such shifts may cause significant changes in the AIT.

Thus it can be seen that the determination of AIT is a very complex problem filled with many potential difficulties. It is only by a study of the fundamental processes of ignition that this complex subject will be understood and that the determination of true AIT values will be possible.

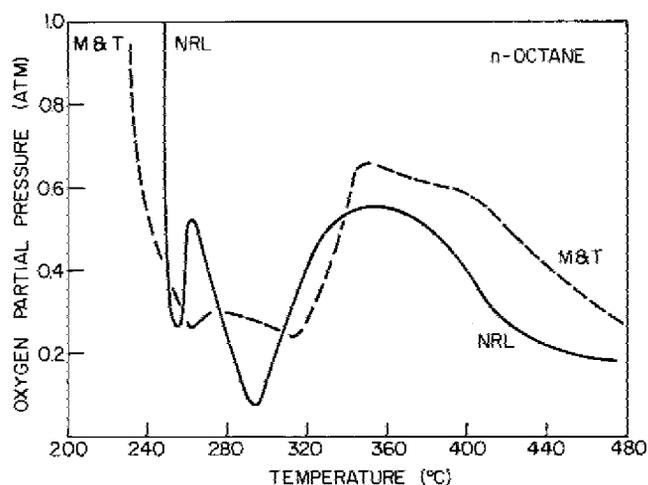


Fig. 7 — Comparison of ignition curves obtained by Maccormac and Townend [16] and NRL work [8]

CONCLUSIONS

Although the autoignition temperature of a substance should be a quantity related to some characteristic chemical property of the material, its experimentally determined value is markedly dependent on the apparatus and method used for its determination. Thus the earlier generalizations concerning the influence of chemical structure on ignition properties are complicated by differences in the methods used for the determinations. For example, the usual determination of autoignition temperatures in air introduces a limiting condition in the ignition curves (such as Fig. 1), as was shown previously. Under this limiting condition, it has been observed that hydrocarbons and related fuels appear to fall into two groups, a low- and a high-temperature ignition region. Zabetakis and coworkers [17], for example, reported the first of these temperature regions to fall below about 290°C and the second above 450°C. They placed long-chain hydrocarbons in the former group and branched short-chain hydrocarbons in the second. If we refer back to

the isomeric hexanes and isooctane ignition curves (Fig. 4), we can see an explanation for this phenomenon. The 21% air line intersects the n-hexane curve in the lower region, but the various branched hydrocarbons shown are intersected in the upper region. As was described previously however changes in apparatus or experimental method can cause shifts in these lobes, so that a compound whose AIT is in one temperature region may be shifted to the other. For this reason, from the viewpoint of safety, there would be a risk if it is assumed that a material with an AIT in the upper region is safe, compared to one in the lower region, since in another environment they both might fall into the same region.

We have seen that there is considerable difficulty in comparing one AIT result with another, even when they are both determined by similar types of apparatus and methods, and that the difficulty increases manifold when the apparatus and methods are not similar. When the concern is with safety, it is of course necessary to go a step further and to extrapolate from laboratory results. The extrapolation of any laboratory results, particularly AIT data, to actual situations is risky. The question arises, can AIT data reliably be extrapolated to outside situations? Can AIT limits be incorporated into military specifications for flammable liquids such as fuels and lubricants for purposes of enhancing ship safety? If there is a possibility of fuel dripping onto a hot steam pipe, can the AIT of the fuel be used to evaluate the potential hazard? Does the AIT of a hydraulic fluid give information regarding the hazards of its use in hydraulic elevators on aircraft carriers? Would it be feasible to replace awkward compression-ignition tests with AIT laboratory tests to evaluate hydraulic fluids? The answer to these questions is a qualified yes, with a provision that more research and knowledge concerning the many ignition phenomena are necessary before realistic interpretations of laboratory data may be made.

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GLOSSARY

Combustion — Any exothermic chemical oxidation process, commonly the rapid chemical union of a substance (combustible) with oxygen. Combustion is accompanied by the evolution of heat and light and sometimes also of sound.

Ignition — The act or process of initiating combustion as evidenced by a glow, flame, or explosion. It is the initiation of visible and/or audible combustion observable under ordinary or specified laboratory conditions.

Autoignition — The ignition of a combustible material, commonly with air, in contact with a large heated surface (or enclosed in a heated vessel) as a result of heat liberation from exothermic oxidation reactions at a sufficient rate and temperature rise but without the aid of an external energy source such as a spark or flame. It is also referred to as "spontaneous ignition" or *autogenous ignition*.

Autoignition temperature — The minimum temperature at which a combustible vapor with air will ignite spontaneously in the experimental apparatus employed. It is that temperature to which a combustible mixture must be raised so that the rate of heat evolved by the exothermic oxidation reactions of the system will just overbalance the rate at which heat is lost to the surroundings. It is also referred to as *spontaneous ignition temperature (SIT)*, or *autogenous ignition temperature (AIT)*. The *minimum* temperature is always implied.

Hot-surface ignition temperature — The lowest temperature at which a specified hot surface will ignite a droplet of fuel which is allowed to fall upon it. Hot-surface ignition temperatures are not as reliable as conventional autoignition temperature values and are usually much higher because of uncontrolled loss of vapor and heat after the droplet hits the hot surface.

Ignition delay — Time interval from contact of an oxidant with a combustible until ignition occurs. It is also referred to as *ignition lag*.

Cool flame — A faint, pale-blue luminescence or flame which occurs at low temperatures in rich vapor-air mixtures of most hydrocarbons and oxygenated hydrocarbons. The visible emission is due solely to electronically excited formaldehyde. The chemistry, which involves chain branching, is not accompanied by a large heat release. Cool flames are the first part of the three-stage ignition process.

Blue flame — The second visible stage of three-stage ignition, which follows the cool flame, is more intense, and is also attributed to electronically excited formaldehyde. Upon an increase in oxygen concentration, this flame can change color to greenish-blue and is then called the *transition flame*. In the latter case, the luminescence is due to other species in addition to formaldehyde.

Three-stage ignition — A separated three-stage flame process in which the initiation of the second stage (blue flame) depends on the products of the first stage (cool flame) and the initiation of the third stage (normal or hot flame) depends on the products of the second stage.

Spontaneous heating — A rise in temperature above ambient of a liquid or solid material as a result of heat liberation due to exothermic chemical reactions within the material itself, or with other reactants, but usually with oxidants such as oxygen or air. The temperature rise must take place without the aid of external energy sources such as flames, sparks, radiant energy, hot surfaces, and the like. This process, which is typified by a drying oil-soaked rag, is also referred to as *self-heating* or *spontaneous combustion*. Spontaneous heating may lead to spontaneous ignition.

Spontaneous heating temperature — The minimum temperature at which a combustible liquid or solid will ignite as a result of spontaneous heating. It is also referred to as *self-heating temperature* or *spontaneous combustion temperature*. The minimum temperature is always implied.

Kindling temperature — The minimum temperature at which a solid combustible can be ignited by an ignition source; it depends on the nature, physical state, size, shape, and chemical composition of the material.